

Limitations of Density Functional Theory in Application to Degenerate States

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ABSTRACT

It is shown that the claims that density functional theory (DFT) can handle orbitally degenerate states are ungrounded. The constraint search formulation of DFT allows one to determine a set of densities and eigenvalues for the degenerate term that, however, are neither observables, nor can they be used to solve the system of coupled equations for the nuclear motions to obtain observables, as in the wave function presentation. A striking example of the failure of the existing versions of DFT to describe degenerate states is provided by the Berry phase problem: the strong dependence of the results on the phase properties of the electronic wave function that are smeared out in the density formulation. The solution of the Jahn–Teller E–e problem illustrates these statements. For nondegenerate states with the full wave function taken in the adiabatic approximation as a product of the electronic and nuclear parts, the formulation of DFT is rigorous if and only if the dependence of the electronic wave function on nuclear coordinates is ignored. This lowers the accuracy of the results, in general, and may lead to erroneous presentation as in the case of molecular systems in strong magnetic fields. © 1997 by John Wiley & Sons, Inc.

Introduction

The density functional theory (DFT) reached a level of widespread use in electronic structure calculations of atoms, molecules, and solids (see ref. 1–6 and references therein). This makes

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most important to explore the possible limitations of the applicability of the existing versions of the theory to various specific problems.

The main assumption of DFT is that the electron–nuclear $V'(q, Q)$ and nuclear–nuclear $V''(Q)$ interactions, $V(q, Q) = V'(q, Q) + V''(Q)$, where q and Q stand for all the electron and nuclear coordinates, respectively, may be regarded as an “external potential” to the electronic subsystem of the

polyatomic system. Under this assumption, the Hohenberg–Kohn (HK) theorem⁷ establishes a one to one correspondence between the electronic density ρ of the ground state and the potential V , and hence between ρ and the energies and wave function of the Hamiltonian H , because the latter is determined by V and the number of electrons that enter ρ by normalization. In the original HK theorem the ground state of the system is assumed to be nondegenerate. This limitation has been formally removed by the Levy–Lieb constraint search formulation^{8,9} in which the density ρ is that of one of the degenerate states, or they are presented by an ensemble density matrix (however, see below).

In the DFT the energy of the ground state is a functional of ρ ,

$$E_0 = E[\rho] = F[\rho] + \int V(q, Q)\rho(q) d\tau, \quad (1)$$

where $F[\rho]$ is a “universal” functional in the sense that it does not depend on V ,

$$F[\rho] = \int \Psi^*(T + U)\Psi d\tau, \quad (2)$$

and T and U are the operators of kinetic and potential energy of the electronic subsystem, Ψ being the ground state wave function associated with ρ . In the Levy–Lieb formulation^{8,9} the true Ψ should minimize ρ .

The possibility of getting complete information about the molecular properties from the ground state density ρ only looks very attractive because ρ is a function in 3-dimensional (3-D) space, and it is thus much more simple than the wave function of a polyatomic system, a function of the coordinates and spins of all the electrons. Therefore, provided ρ can be determined without calculating the wave function (in principle, it can be determined experimentally), the problem of electronic structure of many-electron systems is, in general, simpler in the DFT than in the usual molecular orbital (MO) or valence bond (VB) theories that require multideterminant presentation of the wave function. The work of Kohn and Sham¹⁰ as well as many consequent articles (see refs. 1–6 and references therein) provided practical guides for the solution of the DFT equations for electronic densities that proved to be most efficient. At present DFT is widely used for electronic structure calcula-

tions that in essence are of *ab initio* type, but with model exchange-correlation potentials^{1–6,11}.

However, it seems unlikely that the Schrodinger wave function Ψ contains waste information. This means that the description by multidimensional Ψ can hardly be reduced to the 3-D case without loss of information about the system. As stated by N. March (private commun.), this loss of information is intentional: if properly managed, it simplifies the calculations without loss of accuracy for the corresponding results. But then one must know explicitly what kind of information is lost and how it influences the DFT and the limits of its applicability. Some limitations of DFT were mentioned in the literature (e.g., the failure to describe term multiplicity).

In the present work we discuss briefly some seemingly important basic principles that show that DFT calculations may be inapplicable to specific problems in which the nuclear coordinates must be introduced explicitly. It is shown that in contrast to many claims in the literature (see refs. 1–6, 8, and 11 and references therein), DFT cannot be applied to orbital degenerate and pseudodegenerate states because in these states the electronic and nuclear motions are nonseparable and cannot be described by appropriate densities. Formally, the degenerate-state densities and their corresponding eigenvalues as functions of nuclear coordinates (adiabatic potentials) can be obtained by the Levy–Lieb formulation of DFT; but they are not observables and they cannot be used to solve the equations of nuclear motions to obtain observables, as in the wave function presentation. A striking illustration of the failure of the existing versions of DFT to describe degenerate states is provided by the Berry phase problem^{12–16}: the strong dependence of the resulting energy spectrum and wave functions of the degenerate term on the phase properties of the electronic wave function. The wave function phase information is important also for nondegenerate states, for instance, in the presence of strong magnetic fields.¹⁶ The wave function phase problem is excluded from the density formulation.

In what follows we demonstrate these statements using the well-known system of coupled equations for the problem of a degenerate term. It is shown that the existing versions of DFT cannot be used to solve these equations. For nondegenerate states in the adiabatic approximation the DFT

equations are rigorous if and only if the dependence of the electronic wave function on nuclear coordinates is ignored. This lowers the accuracy of the results, in general, and may lead to erroneous presentations in special cases.

Nondegenerate States: Born–Oppenheimer and Full Adiabatic Approximations

Consider first a polyatomic system in a given nuclear configuration with an isolated nondegenerate electronic term. In the DFT, beginning with its basic HK theorem, the nuclei are considered fixed. Formally this limitation can be eliminated by introducing the nuclear wave function and nuclear density. In the work of Capitani and colleagues¹⁷ the so-called non-Born–Oppenheimer situation in DFT is considered by introducing the nuclear density that is treated on the same level as the electronic density, assuming that the total wave function is multiplicative with respect to the electronic and nuclear coordinates. In somewhat different terminology (see, e.g., refs. 18 and 19) both the Born–Oppenheimer crude adiabatic (CA) and the full adiabatic (FA) approximations assume the multiplicative form of the wave function; in the CA approximation the electronic function is independent of nuclear coordinates, while in the FA case the electronic function contains the nuclear coordinates as parameters. From this point of view this article¹⁷ deals with the CA approximation. As seen from the discussion below, if the nuclear coordinates are included explicitly, the difference between the CA and FA approximations is significant in the DFT formulation. In the study of Carr and Parrinello²⁰ in which a combination of DFT and molecular dynamics is used to consider nuclear dynamics problems, the electronic and nuclear motions are fully separated in the CA approximation.

In the CA approximation the full wave function is a product of the electronic $\varphi(q)$ and nuclear $\chi(Q)$ functions

$$\Psi(q, Q) = \varphi(q)\chi(Q), \quad (3)$$

and both $\varphi(q)$ and $\chi(Q)$ are orthonormalized. With this function and using the usual definition, the electronic and nuclear densities are

$$\rho(\mathbf{r}) = \int |\Psi|^2 d\tau_Q d\tau_q / d\mathbf{r} = \int |\varphi(q)|^2 d\tau_q / d\mathbf{r}, \quad (4)$$

$$\rho(\mathbf{R}) = \int |\chi(Q)|^2 d\tau_Q / d\mathbf{R}. \quad (5)$$

The proof of the HK theorem is based on the presentation of the expectation value of the electron–nuclear interaction $V'(q, Q)$ as a functional of ρ [the nuclear–nuclear interaction $V''(Q)$ is not important in the discussion below]. With the wave function (3) this can be done straightforwardly, provided the problem is formulated with respect to the electronic density and the densities of each of the nuclei.¹⁷

In the FA approximation

$$\Psi(q, Q) = \varphi(q, Q)\chi(Q), \quad (6)$$

and the formula for the electronic density modifies

$$\rho(\mathbf{r}) = \int |\chi(Q)|^2 |\varphi(q, Q)|^2 d\tau_Q d\tau_q / d\mathbf{r}, \quad (7)$$

while the expression for the nuclear density (5) remains unchanged. It is seen from eq. (7) that, unlike the CA approximation, in the FA treatment the nuclear wave function does not disappear from the expression of the electronic density. This complicates the presentation of the energy as a functional of the densities. For the electron–nuclear interaction $V'(q, Q)$, which is an additive function of electronic coordinates \mathbf{r}_i , as well as of nuclear coordinates \mathbf{R}_j , $V' = \sum_{i,j} v(\mathbf{r}_i, \mathbf{R}_j)$, the expectation value is

$$\begin{aligned} & \int V'(q, Q) |\Psi|^2 d\tau_Q d\tau_q \\ &= \sum_{i,j} \int v(\mathbf{r}_i, \mathbf{R}_j) |\chi(Q)|^2 |\varphi(q, Q)|^2 d\tau_Q d\tau_q. \end{aligned} \quad (8)$$

In the CA approximation $\varphi(q, Q) = \varphi(q, Q_0)$, and integration first over $d\tau_q / d\mathbf{r}_i$ and then over $d\tau_q / d\mathbf{R}_j$ yields

$$\begin{aligned} & \int V(q, Q) |\Psi|^2 d\tau_Q d\tau_q \\ &= \sum_{i,j} \int v(\mathbf{r}_i, \mathbf{R}_j) \rho(\mathbf{r}_i) \rho(\mathbf{R}_j) d\mathbf{r}_i d\mathbf{R}_j, \end{aligned} \quad (9)$$

where $\rho(\mathbf{r}_i)$ and $\rho(\mathbf{R}_j)$ are the electronic and nuclear densities, respectively, given in eqs. (4) and

(5). This corresponds to the rigorous DFT presentation: based on eq. (9), the energy of the system is a functional of the electronic and nuclear densities.

However, in the FA approximation the integration in the right-hand side of (8) cannot be performed to yield the corresponding densities because of the dependence of the electronic function on nuclear coordinates. Similarly, presenting the total Hamiltonian as a sum of three parts

$$H = H(q) + V(q, Q) + T(Q), \quad (10)$$

where $H(q)$ is the electronic part and $T(Q) = -\hbar^2 \sum_i (2M_i)^{-1} \partial^2 / \partial Q^2$ is the nuclear kinetic energy, one can see that the full energy of the system

$$E = \langle \chi(Q) \varphi(q, Q) | H(q) + V(q, Q) + T(Q) | \varphi(q, Q) \chi(Q) \rangle, \quad (11)$$

is also not a functional of the densities. In addition to the electron–nuclear interaction term (8) (which is not a functional of densities), there is a nonadiabatic contribution from the T operator that may be very important in special cases (see below).

It follows that the rigorous DFT formulation is based on the crude adiabatic approximation that ignores the dependence of the electronic wave function on nuclear coordinates. This means that the DFT presentation is approximately even for systems with nondegenerate electronic states. The CA approximation is hardly acceptable in cases when the nuclear motions are significant. Indeed, even in simple vibrational problems the parameter of smallness that determines the accuracy of the calculations is $(m/M)^{1/4} \approx 0.15$ in the CA approximation and $(m/M)^{3/4} \approx 0.003$ in the FA approximation.¹⁸

But much more impressive is the fact that the CA approximation (on which the rigorous formulation of DFT is based) loses important physical observables. For instance, for molecular systems in strong magnetic fields the expectation value of the nonadiabatic contribution to the energy [i.e., the terms that remain in eq. (11) after integration over the electronic coordinates q with the magnetic field included in the Hamiltonian; see the off-diagonal terms of the nonadiabatic interaction in eq. (15) below], which is ignored in the CA approximation, contains the screening of the nuclei against the magnetic field.^{21,22} This means that the DFT-based calculations ignore the electronic screening of the nuclei in magnetic fields; this in turn yields divergent paramagnetic and diamagnetic energies

in the dissociation limit.²² This important magnetic field effect is also related to the Berry phase problem,¹⁶ which is thus significant also for nondegenerate states.

ELECTRONIC DEGENERACY AND PSEUDODEGENERACY

The case of electron degeneracy is of particular importance to the problem discussed here because of the special coupling between the electronic and nuclear motions that makes them nonseparable and the breakdown of the adiabatic approximation.^{18,19} As mentioned above, in the original HK theorem⁷ the ground state was assumed to be nondegenerate, but with the Levy–Lieb constraint search formulation^{8,9} all the consequent articles on this subject claim that the DFT is applicable to degenerate states as well. Indeed, in this formulation all the f electronic densities of the f -fold degenerate state can be defined, in principle, for fixed nuclear configurations. However, distinct from the nondegenerate state, for $f > 1$ these electronic densities (or the ensemble density matrix) have no independent physical sense, they are not observable, and they do not determine the charge distribution and energy spectrum of the system. Note that the same is true for the wave functions and eigenvalues of a degenerate state obtained for fixed nuclei.

For illustration of these statements, the well-known formulation of the vibronic problem for an f -fold degenerate term is presented. Consider a polyatomic system with the Hamiltonian (10) and assume first that the kinetic energy of the nuclei $T(Q)$ can be ignored. Then the electronic equation for a fixed-nuclei configuration Q is

$$[H(q) + V(q, Q)] \varphi_n(q, Q) = \varepsilon_n(Q) \varphi_n(q, Q). \quad (12)$$

The exact eigenfunction of the system can be sought for in the form of an expansion over the full system of the electronic functions $\varphi_n(q, Q)$,

$$\Psi = \sum_n \chi_n(Q) \varphi_n(q, Q), \quad (13)$$

where the coefficients χ_n are functions of Q . By substituting (13) into the Schrodinger equation with the Hamiltonian (10), we come to the following infinite system of coupled equations with re-

gard to $\chi(Q)$.

$$[T(Q) + \varepsilon_m(Q) - E] \chi_m(Q) + \sum_{n \neq m} \Lambda_{mn}(Q) \chi_n(Q) = 0, \quad (14)$$

$$m = 1, 2, \dots$$

where

$$\Lambda_{mn}(Q) = h^2 \sum_i M_i^{-1} [A_{mn}^{(i)} \partial / \partial Q_i + B_{mn}^{(i)}(Q_i)], \quad (15)$$

$$A_{mn}^{(i)} = \int \varphi_m^* \partial \varphi_n / \partial Q_i d\tau,$$

$$B_{mn}^{(i)} = (1/2) \int \varphi_m^* \partial^2 \varphi_n / \partial Q_i^2 d\tau, \quad (16)$$

and $\varepsilon_m(Q)$ are eigenvalues of (12).

If the off-diagonal terms with Λ_{mn} are small and can be neglected, the system of eq. (14) uncouples, and we get separate equations for each of the independent functions $\chi_n(Q)$ describing the ground and excited vibrational states of the electronic state $\varphi_n(r, Q)$. This is the full adiabatic approximation mentioned above. The wave function (13) for each electron-vibrational state in this case is multiplicative, $\Psi_{nm}(q, Q) = \varphi_n(q, Q) \chi_m(Q)$, and the DFT (in the sense of electronic and nuclear densities¹⁷) can be formulated approximately, provided the dependence of the electronic function $\varphi_n(q, Q)$ on Q can be ignored.

However, if in eq. (12) for some value $Q = Q_0$ there are $f > 1$ states $\varphi_n(q, Q)$, $n = 1, 2, \dots, f$, for which $\varepsilon_1(Q_0) = \varepsilon_2(Q_0) = \dots = \varepsilon_f(Q_0)$ (electronic f -fold degeneracy), then the off-diagonal elements $\Lambda_{mn}(Q_0)$ within this manifold cannot be ignored. They are of the same order of magnitude as the remaining terms in eq. (14). If this degenerate term is well separated from other terms, then in the same approximation as the above adiabatic one, we can ignore the coupling to distant terms and reduce the infinite system (14) to f coupled equations of the f -fold term. Quite similar coupled equations occur for pseudodegenerate electronic states for which the $\Lambda_{mn}(Q)$ terms that mix ground and excited states cannot be ignored.^{18,19}

As mentioned above, neither $\varepsilon_m(Q)$ nor the φ_n functions have any physical sense of observables [for well-separated sheets each of the functions $\varepsilon_m(Q)$ has the meaning of the potential energy of the nuclei in the field of the electron], and only the solution of eq. (14) yields the corresponding energy spectrum and wave functions. However, the

DFT formulation of the problem, at least in the form of the DFT known so far, does not allow for the solution of eq. (14), mainly because the off-diagonal elements Λ_{mn} cannot be presented by densities. The solution of the problem of degenerate states by DFT methods stops at the solution of electronic eq. (12) and cannot go any further. With the wave function (13) the electronic density is

$$\rho(\mathbf{r}) = \int \left| \sum_n \chi_n(Q) \varphi_n(q, Q) \right|^2 d\tau_Q d\tau_q / d\mathbf{r}, \quad (17)$$

and the expectation value of the electron-nuclear interactions

$$\begin{aligned} & \int V(q, Q) |\Psi|^2 d\tau_q d\tau_Q \\ &= \sum_{i,j} \int v(\mathbf{r}_i, \mathbf{R}_j) \left| \sum_n \chi_n(Q) \varphi_n(q, Q) \right|^2 d\tau_q d\tau_Q \end{aligned} \quad (18)$$

cannot be presented as a functional of ρ .

It follows that, distinguished from the nondegenerate case where the DFT formulation is still possible approximately by ignoring the dependence of φ on Q , in the case of electronic degeneracy such a formulation is impossible, even approximately. Thus, the currently known versions of DFT are inapplicable to polyatomic systems in electronic degenerate states and when there are close in energy states that mix strongly enough under nuclear displacements. The criterion of strong vibronic mixing is given in refs. 18 and 19.

The special coupling between the electronic and nuclear motions in the case of orbital degeneracy, in addition to making the full wave function nonmultiplicative, imposes some peculiar conditions on the wave function phase; one of them is known as the Berry phase problem (see refs. 12–16 and references therein). Because the density does not contain any wave function phase information, the DFT cannot handle this problem, in principle. The solution of the Jahn–Teller E–e problem, given below, allows a better understanding of this statement.

EXAMPLE: THE LINEAR E–e PROBLEM

To illustrate the main statements of this note and to make them more specific, in particular, to disclose the meaning of the Berry phase problem, we present here the solution of the well-known

and widely studied Jahn–Teller E–e problem, a twofold degenerate electronic term E interacting with twofold degenerate symmetrized nuclear E displacements Q_θ and Q_ϵ .^{18,19} Taking into account the linear and quadratic terms of vibronic coupling that also involve the totally symmetric displacements Q_A , one can obtain the following form of the two sheets of the adiabatic potential²³:

$$\begin{aligned}\varepsilon_\pm(\rho'_A, \rho', \phi) &= (1/2)K_A \rho'^2_A - F_A \rho'_A + (1/2)K \rho'^2 \\ &\pm \rho' \left[F^2 + G^2 \rho'^2 \right. \\ &\left. + 2FG(\rho' \cos 3\phi - \sqrt{2}\rho'_A) \right. \\ &\left. + 4G^2 \rho'^2_A (2\rho'_A - \sqrt{2}\rho' \cos 3\phi) \right]^{1/2}.\end{aligned}\quad (19)$$

Here F and G are the linear and quadratic vibronic constants of coupling to the e displacements $Q_\theta = \rho' \cos \phi$ and $Q_\epsilon = \rho' \sin \phi$, where ρ' (not to be confused with the density ρ !) and ϕ are polar coordinates; $K = M\omega^2$ is the corresponding bare (nonvibronic) force constant; and F_A and K_A are, respectively, the vibronic and force constants for totally symmetric displacements ρ'_A .

For the sake of simplicity we assume that the quadratic coupling is small, $G \approx 0$. Then the totally symmetric displacements can be separated and

$$\varepsilon_\pm(\rho', \phi) = (1/2)K \rho'^2 \pm |F| \rho'. \quad (20)$$

For the wave functions, ignoring the dependence of the $\varphi(q, Q)$ functions on the nuclear coordinates Q (which is equivalent to the CA approximation in the nondegenerate case), we have

$$\begin{aligned}\psi_- &= \cos(\phi/2)\varphi_1(q, Q_0) - \sin(\phi/2)\varphi_2(q, Q_0), \\ \psi_+ &= \sin(\phi/2)\varphi_1(q, Q_0) + \cos(\phi/2)\varphi_2(q, Q_0),\end{aligned}\quad (21)$$

where φ_1 and φ_2 are the two electronic wave functions that realize the electronic degeneracy at $Q = Q_0$ (e.g., the d_{z^2} and $d_{x^2-y^2}$ atomic functions of a transition metal in a cubic environment).

Equation (20) is a surface of revolution (the “Mexican hat”) illustrated in Figure 1 together with the nuclear configuration of an octahedral system in several points along the bottom of the

trough of this surface. By solving one of the equations of the system of two equations (14) with this potential under the assumption that the vibronic coupling is strong enough, one gets the following solutions for the low-energy states of the lower sheet $\varepsilon_-(\rho', \phi)$:

$$\Psi_{nm}(q, \rho', \phi) = \psi_-(q, \rho', \phi) \chi_n(\rho' - \rho'_0) \times \exp(im\phi)/(2\pi\rho')^{1/2}, \quad (22)$$

$$\begin{aligned}E_{nm} &= h\omega(n + 1/2) + m^2(h\omega)^2/4E_{JT} - E_{JT} \\ n &= 1, 2, \dots; \quad m = \pm 1/2, \pm 3/2, \pm 5/2, \dots,\end{aligned}\quad (23)$$

where E_{JT} is the Jahn–Teller stabilization energy,

$$E_{JT} = F^2/K, \quad (24)$$

ρ'_0 is the radius of the trough,

$$\rho'_0 = |F|/K, \quad (25)$$

ψ_- is given by eq. (21), and $\chi_n(\rho' - \rho'_0)/(2\pi\rho')^{1/2}$ is the vibrational function for the transversal (to the trough) vibrations along ρ' .

Equation (22) and Figure 1 show explicitly that even in this most simplified situation there is a special coupling between the electronic and nuclear motions that makes the wave function of the electron and nuclei nonmultiplicative. In this simple case in the approximation of fixed nuclei in the electronic functions, the electronic density is

$$\rho(\mathbf{r}) = (1/2) \left[|\varphi_1(\mathbf{r}, Q_0)|^2 + |\varphi_2(\mathbf{r}, Q_0)|^2 \right], \quad (26)$$

while the nuclear density is independent of ϕ

$$\rho(\rho', \phi) = |\chi(\rho' - \rho'_0)|^2. \quad (27)$$

With these densities, by substituting the wave function (22) into eq. (18), one gets a complicated expression that cannot be reduced to a functional of $\rho(\mathbf{r})$ and $\rho(\rho')$.

An important feature of solutions (22) and (23) is that the quantum number m must be a half-integer. This result emerges from a very peculiar property of the phase of the electronic wave function. As one can easily find out from eq. (21), the electronic functions $\psi_\pm(\rho', \phi)$ are not uniquely defined in the space of nuclear coordinates because of the relation $\psi(\phi + 2\pi) = -\psi$. This con-

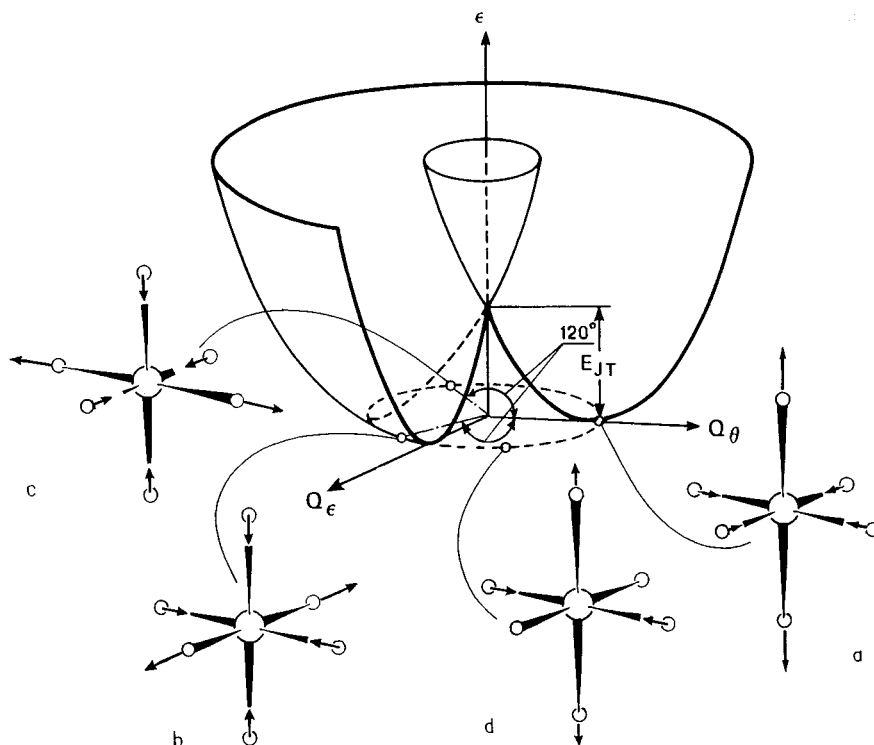


FIGURE 1. Illustration to the nonseparable electron–nuclear motions in degenerate states: the adiabatic potential surface of a twofold degenerate electronic E term in the space of the nuclear e displacements Q_θ and Q_ϵ in the linear approximation (the “Mexican hat”). Along the bottom of the trough the electronic density changes continuously together with the nuclear configuration: at (a) $\phi = 0$, (b) 120° , and (c) 240° the octahedron is tetragonally elongated along the three fourfold axes, respectively, while (d) in between all three diagonals of the octahedron have different lengths.

dition has some interesting consequences known as the Berry phase problem.^{12–16} To obey the requirement that the full wave function should be uniquely defined, the quantum number m in (22) must be a half-integer, and this requirement significantly changes the energy spectrum and wave functions. Similar phase effects occur in other degenerate states.

Another example where the wave function phase effect is essential is concerned with the above-mentioned molecular systems in strong magnetic fields.^{21,22} The electronic screening of the nuclei against the magnetic field is shown to be related to the wave function phase problem.¹⁶ Obviously, these and other special wave function phase effects, including the Berry phase, cannot be reproduced in the DFT description because the electronic and nuclear densities do not contain information about wave function phases.

Conclusion

In essence, DFT uses a reasonably reduced description of molecular systems by “contracting” the multivariable wave function to a 3-D electronic density, and this procedure proved to be practically very efficient in electronic structure calculations of energies and some other physical quantities. This contraction may result in loss of information about the system, and the problem is thus to find out what molecular properties can be affected by such a contracted description. It was shown that nuclear motions cannot be properly incorporated in the existing versions of DFT. This is especially important for orbitally degenerate and pseudodegenerate states for which the electronic and nuclear motions are nonseparable. The problem of

strong wave function phase effects is most illustrative in this respect. For nondegenerate states, the CA separation of the electronic and nuclear motions makes the DFT description approximate, in general, and invalid in special cases, for instance, when considering molecular systems in strong magnetic fields.

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References

1. R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford Univ. Press, New York, 1989.
2. N. H. March, *Electron Density Theory of Atoms and Molecules*, Academic Press, New York, 1992.
3. S. B. Trickey, *Adv. Quantum Chem.*, **21** (1990).
4. J. K. Labanowski and J. W. Andzelm, Eds., *Density Functional Methods in Chemistry*, Springer, New York, 1991.
5. J. Weber, *New J. Chem.*, **16**, N12 (1992).
6. E. S. Kryachko and E. V. Ludena, *Energy Density Functional Theory of Many-Electron Systems*, Kluwer, Dordrecht, 1990.
7. P. Hohenberg and W. Kohn, *Phys. Rev.*, **136**, B846 (1964).
8. M. Levy, *Proc. Natl. Acad. Sci. USA*, **76**, 6062 (1979); *Phys. Rev.*, **A26**, 1200 (1982).
9. E. Lieb, *Int. J. Quantum Chem.*, **24**, 243 (1983).
10. W. Kohn and L. J. Sham, *Phys. Rev.*, **140**, A1133 (1965).
11. D. R. Salahub, In *Metal-Ligand Interactions: From Atoms, to Clusters, to Surfaces*, D. R. Salahub and Nino Russo, Eds., Kluwer, Dordrecht, 1992.
12. M. V. Berry, *Proc. Roy. Soc. (Lond)*, **A392**, 45 (1984).
13. R. Jackiw, *Comments Atom. Mol. Phys.*, **21**, 71 (1988).
14. S. E. Apsel, C. C. Chancey, and M. C. M. O'Brien, *Phys. Rev. B*, **45**, 5251 (1992).
15. B. R. Judd, In *Vibronic Processes in Inorganic Chemistry*, C. D. Flint, Ed., Kluwer, Dordrecht, 1989, p. 79.
16. C. A. Mead, *Rev. Mod. Phys.*, **64**, 51 (1992).
17. J. F. Capitani, R. F. Nalewajski, and R. G. Parr, *J. Chem. Phys.*, **76**, 568 (1982).
18. I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer, New York, 1989.
19. (a) R. Englman, *The Jahn-Teller Effect in Molecules and Crystals*, (Wiley, New York, 1972); (b) I. B. Bersuker, *The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry*, Plenum, New York, 1984; (c) G. Fischer, *Vibronic Coupling: The Interaction Between the Electronic and Nuclear Motions*, Academic Press, London, 1984; (d) C. D. Flint, Ed., *Vibronic Processes in Inorganic Chemistry*, Kluwer, Dordrecht, 1989; (e) I. B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds. Introduction to the Theory*, Wiley, New York, 1996.
20. R. Carr and M. Parrinello, *Phys. Rev. Lett.*, **55**, 2471 (1985).
21. P. Schmelcher, L. S. Cederbaum, and H. D. Meyer, *J. Phys. B*, **21**, L445 (1988).
22. P. Schmelcher, L. S. Cederbaum, and H. D. Meyer, *Phys. Rev. A*, **38**, 6066 (1988).
23. A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (USA)*, **3**, 304 (1958).